The aluminium-copper-gold ternary system

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Abstract

Despite Au, Al and Cu being individually very well-known elements, their ternary phase diagram has not been studied in as much detail as those of many other Au-containing ternaries. Here we review what is known, and consider the prospects for technological exploitation of some of the ternary compositions. The components of greatest interest in Al-Au-Cu may be the β-phases, at least two of which have shape memory properties. Of these, 'Spangold', which has the nominal stoichiometry $Au_7Cu_5Al_4$, has received some attention for jewellery applications, while the edge compound Cu_3Al is a well-known shape memory composition with corresponding specialised industrial uses. The properties of other β-phase compositions in the system have been scarcely investigated. The system also contains an extensive γ-phase, $Al_4Au_xCu_{9-x}$, where x ranges from 0 to ~6.5, and the purple gold phase $AuAl_2$.

Introduction

Most gold alloys in current commercial use contain additions of copper, silver and zinc. For this reason, ternary phase diagrams of those systems have been available for several decades. However, there seems to have been only scanty interest in the gold-copper-aluminium system prior to the 1990s. Furthermore, no phase diagram of this system was provided in the various authoritative monographs published in that decade [1, 2]. This is surprising given that gold, aluminium and copper are such well known face centred cubic (fcc) metals. To remedy this apparent omission Levey and Cortie investigated both the 500°C isothermal and 18 carat pseudo-binary sections of this system [3, 4] with their conclusions being subsequently assessed and summarised by Raghavan [5]. However, the few articles cited above merely hint at the fascinating complexity of this ternary system and further publications have, in the interim, also appeared. In the present review we discuss what is now known, both in terms of the phase diagram, and in terms of technological applications, and will show where further research is required.

Of course, the edge binary systems of the ternary are certainly well known and are given in many compendia of phase diagrams. Copper-gold, which forms a continuous range of fcc solid solutions at elevated temperatures, has been exploited since ancient times [6] due to its natural occurrence and attractive reddish colour. Its binary phase diagram has been intensively investigated, primarily because its high temperature α-(Au,Cu) solid solution undergoes various interesting structural transformations at lower temperatures. Similarly, the aluminium-copper system has been thoroughly studied. It contains a series of intermetallic compounds, some of which are classic Hume-Rothery electron phases. The β-phase electron compound Cu_3Al, in particular, has been examined in some detail because it has shape-memory properties. Finally, like Al-Cu, the aluminium-gold system also contains a series of intermetallic compounds. Of these, the purple gold intermetallic compound $AuAl_2$, attracted attention over a century ago [7] and has been intermittently investigated since then (see Supansomboon et al. and references therein [8]) while the unstable β-phase (nominally Au_9Al_2) and its peculiar metastable relationship to the intermetallic compound Au_4Al have also been considered [9, 10].

Although there were some early forays into the ternary system of Au, Al and Cu, the results were contradictory and confusing. At least three groups have examined the effect of systematic additions of Al to equiatomic α-(Au,Cu). Raub and Walter, for example, added up to 1.8 wt% Al to equiatomic (Au,Cu) and noted that a small proportion of a second phase with a structure similar to "Au_3Al" precipitated [11] (it can be deduced from the context that they meant the β-phase Au_9Al_2 electron compound mentioned above). Isobe, on the other hand added between 2 and 4% Al (by weight) to

nominally equiatomic (Au,Cu) and concluded that a β-phase formed if the composition was heat treated at 400°C [12] but that this β-phase was different to the one on the Al-Au edge. In contrast, Sato and Toth [13] added up to 23 atomic % Al to AuCu thin films, but reported (in what has proved to be very well cited paper over the years) that the structure of the resulting material was related to that of AuCu-II (which is a superlattice derived from fcc α-(Au,Cu). The effect of Al additions to $AuCu_3$ has also been examined. For example, Chapman and Gillam added up to 2.5 atomic % (0.37 wt %) Al to $AuCu_3$ and discovered that this caused additional ternary ordering, indicated by the presence of well-defined "side-bands" (extra lines next to the lines of the original diffraction pattern) and anomalous effects on the mechanical properties [14].

Ternary alloys of gold, copper and aluminium appear to have been first investigated for their potential technological applications in the 1970s. For example, an entry in *Chemical Abstracts* alludes to a Au-Cu-Al alloy containing 1.1-5.0% Al and 7.1-4.9% Cu with optional additional elements which was developed for springs, prosthetics and decoration due to its high strength combined with castability and workability [15]. In another development, it was found that small additions of Al to a 22 carat Au-Cu alloy decreased its hardness and colour intensity [16]. In the 1990s there was interest in using Au-Al-Cu alloys in shape memory alloys [12], dentistry (as an age-hardening composition) [17], or jewellery [18, 19]. One of these compositions, often described as 'Spangold', is capable of developing a magnificent sparkling surface texture after appropriate processing, and an attempt was made to develop it as a jewellery alloy [18, 19]. The texture is caused by inducing a martensitic-type phase transformation to take place within a sample with a polished surface. Transformations of this type are characterised by considerable crystallographic shear and deformation, which causes a previously flat surface to become faceted. The facets then disperse incident light to cause a pleasing aesthetic effect (Figure 1). Spangold is a β-phase alloy with a nominal stoichiometry of $Au_7Cu_5Al_4$ and a nominal composition of 76% Au, 18% Cu, 6% Al by mass [20].

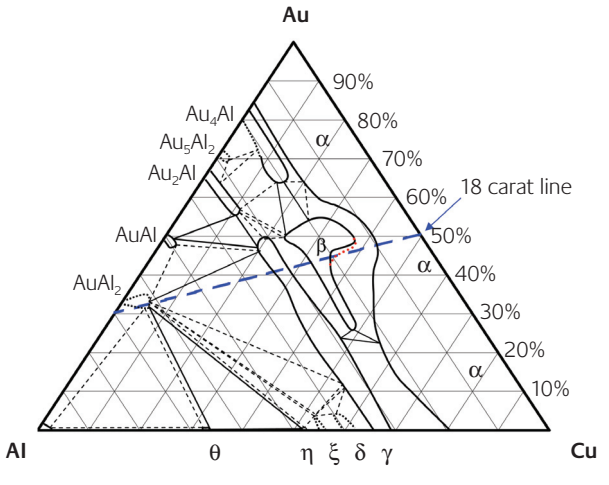
Figure 1

The textured effect produced by a martensitic transformation on the planar surface of a Spangold 'tension bangle' is evident in the reflected image of the ring. (Tension bangle designed and manufactured by jeweller Kurt Donau of Johannesburg, South Africa for exhibition at the 1993 Basel Watch and Jewellery Fair in Switzerland. This work was financially supported in 1993-94 by the World Gold Council and Mintek, South Africa. Photo: M.B. Cortie and F.C. Levey)

Composition and phases

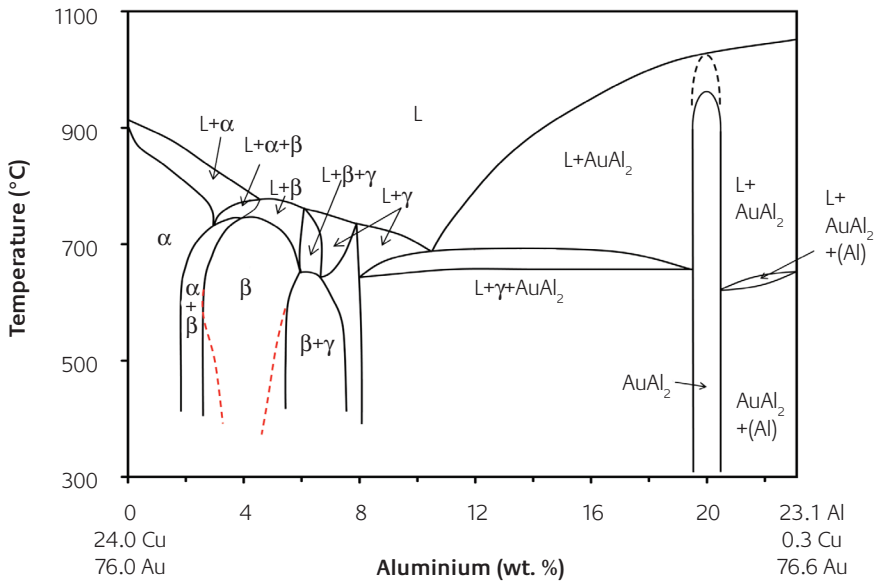
While most of the literature on ternary Al-Au-Cu alloys does focus on the properties of Spangold, there are some limited data on the ternary system itself. A proposed 500°C isothermal section [3] is reproduced in Figure 2 and shows the range of phases and alloys that can be produced from different proportions of the base metals at that temperature. The main aim of that particular work was to define the extent of the β-phase field as it is these compositions that can undergo the reversible martensitic phase transformation. A pseudo-binary binary diagram of 76 wt% Au alloys has also been published [4], Figure 3, which shows the relationships across a temperature range of 400 – 1000°C. This latter

Figure 2



Proposed isothermal section through Al-Au-Cu system at 500°C (reproduced from Levey and Cortie[3]) in atomic percent. The dashed blue line shows the position of the 18 carat isopleth. The dotted red line designates that there is some uncertainty in the position of the β phase boundary in the indicated region

Figure 3



Pseudo-binary section through Al-Au-Cu system at 76 wt.% Au. (Redrawn from Levey et al.[4]). The dotted red lines indicate that prolonged annealing studies are likely to reveal some constriction in the β-phase field at lower temperatures

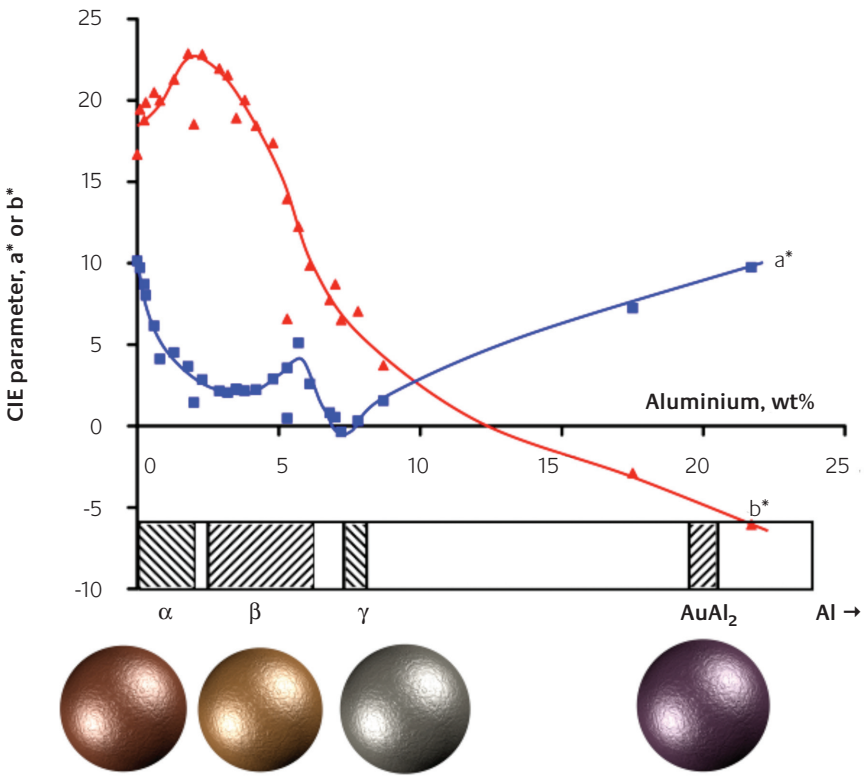
paper provided detailed information on many of the different phases present in the binary diagram and was based on a large number of sample compositions, extending from Au-24 wt% Cu to Au-23 wt% Al-0.3 wt% Cu. However, most β-phase fields are V-shaped on their isopleth sections and we suggest that further work is likely to show this for the Spangold β phase as well. In Figure 3 we indicate this possibility with red dashed lines. Later work by Fumagalli *et al*., confirmed that the β-phase extended from at least 44 to 57.6 at.% Au, and provided data that showed that the enthalpy (and transformation temperatures) of the martensitic transformation increased as the gold content was decreased [21].

In broad summary, it can be seen from the isothermal diagram that the α-phase extends across the entire length of the Cu-Au edge at 500°C, reaching into the ternary diagram to approximately 20 at% Al at the Au and Cu ends and regressing back to approximately 10 at% Al at 50 at% Au. At higher Al and Au contents a ternary β-phase is stable on the 500°C section. This widens considerably at approximately 50 at% Au. The ternary β-phase lies along a line which has an electron-to-atom ratio of 1.48 indicating that it is a Hume-Rothery β-electron compound. It is, however, discontinuous (at 500°C) with the binary β-phase alloy Au_9Al_2. The binary Cu_3Al β-phase would also lie on this line of electron-to-atom ratio but it is not stable below 567°C and is hence absent on the 500°C section [5]. This suggests that at higher temperatures the ternary β-phase might join up with the Cu_3Al and Au_9Al_2 β-phases to form a continuous phase field from the Cu-Al edge to the Au-Al edge of the ternary diagram. Certainly Fumagalli *et al*. found that an as-cast and aged alloy with 57.6 at% Au, 23.1 at.% Cu and 19.3 at% Al was fully β-phase [21] whereas the 500°C section of Levey and Cortie would have this as a three-phase mixture of α, Au_2CuAl and Au_4Al. A continuous β-phase has been observed in other systems, for example Au-Ag-Al where the Au_4Al intermetallic compound stretches across nearly the entire ternary section at 500°C [1]. Further work seems necessary.

The γ-phase extends over half the length of the ternary diagram, forming over a narrow range of Al content at approximately 25-30 at% Al. The phase field follows an electron-to-atom ratio of ~1.61 and is based on the binary γ-phase alloy Al_4Cu_9, with Au substituting for Cu to give the stoichiometry $Al_4Au_xCu_{9-x}$ where 0<x<~6.5. Gamma phases are invariably very brittle and have a complex structure which is usually ordered. The XRD patterns of $Al_4Au_xCu_{9-x}$ show some differences to the standard pattern of Cu_9Al_4, which are attributable to a combination of texturing, non-random substitution of Au for Cu, i.e. a degree of ternary ordering, and an increase in lattice size due to the larger radius of the Au atoms (0.144 nm) compared to the Cu atoms (0.128nm) [3]. Similarly to the β-phase, the γ-phase does not extend all the way to the Al-Au edge, and there is a gap between the ternary γ-phase and the corresponding binary phase Au_2Al.

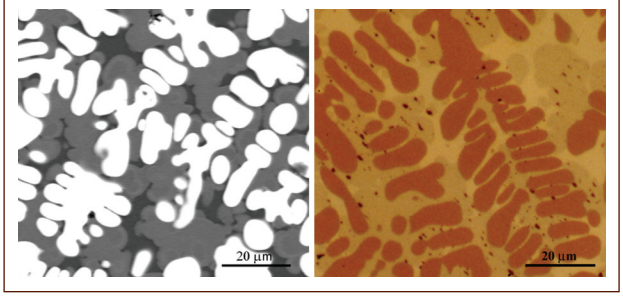
These three phases (α, β and γ) make up the main features of this ternary diagram. However, the intermetallic compounds Au_4Al and Au_2Al also have a significant range of stoichiometry. The rest of the binary edge compounds only extend into the ternary by a few percent. All the known phases are listed by Raghavan [5]. Obviously, regions on the phase diagram in-between the main phases will consist of mixtures of two or three phases. These multi-phase regions account for the largest area of the Al-Au-Cu ternary diagram.

Figure 4



CIE a and b* colour coordinates of alloys along the 18 carat pseudo-binary, and position of phase fields (Colour data and phase boundaries taken from Levey and Cortie[4, 22]. Simulated sample spheres rendered by POVRay software using rgb colours obtained from typical images of the four alloys shown, provided here merely as a visual guide.)*

Figure 5



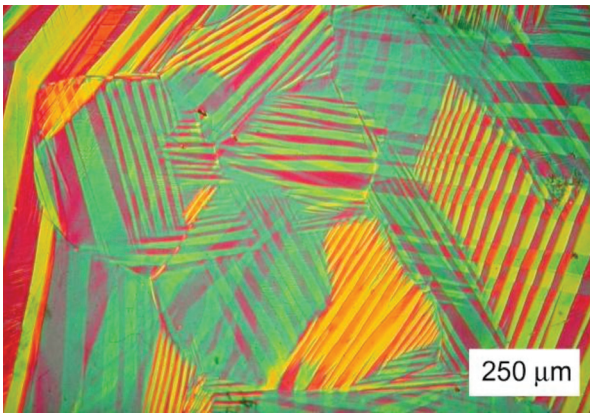
Optical and backscatter scanning electron microscope micrographs of an as-cast sample containing 61 at% Al, 24 at% Cu and 15 at% Au. On the greyscale SEM backscatter image (left) $AuAl_2$ is white, AlCu is light grey and Al_2Cu is dark grey. On the optical microscope image (right) $AuAl_2$ is pink, AlCu is tan, and Al_2Cu is cream (present authors, unpublished work)

Microstructure and colour

Many interesting microstructures have been imaged and documented in the literature on Al-Au-Cu alloys. These include martensitic laths, dendrites, eutectics and massive transformations. Possibly, the most striking example of this variation in microstructure may be found along the 18 carat pseudo-binary [22]. This starts on the Au-Cu edge with α-phase alloys showing a reddish gold colour, but as the Al content is increased this colour fades to yellow, until the composition reaches the β-phase boundary at which point the yellow transitions to a pink/apricot colour. Once the β-phase is replaced by γ the colour is rapidly bleached to silver. However, on proceeding further across the pseudo-binary, $AuAl_2$ forms, which increasingly produces a purple hue, saturating once the alloy was mostly comprised of this compound. Finally, further additions of Al take the system into the Al+$AuAl_2$ phase field, with associated bleaching of the purple. The trends in the CIE *a** and *b** colour parameters are shown in Figure 4.

A notable characteristic of this system is that the microstructures of its multi-phase alloys are easily visualised due to the large difference in both colour and average atomic number. Examples of this are seen in the literature [3, 4, 22] with very intricate structures being observed in both the annealed and as-cast samples. To illustrate this point here we show previously unpublished colour optical and back-scatter SEM micrographs, Figure 5, of a polished sample with a nominal composition of 61 at.% Al, 24% at.% Cu and 15 at.% Au containing the phases $AuAl_2$, CuAl and $CuAl_2$. These phases are respectively pink, tan and yellow under optical conditions, and white, grey and dark grey under SEM

Figure 6



Nomarski interference contrast image of a polished surface of Spangold that has undergone a martensitic transformation (F.C. Levey, Doctoral thesis, 2000, University of Witwatersrand, South Africa)

backscatter imaging. The backscatter images in scanning electron microscopes show large changes in contrast due to the large difference in average atomic number of phases present due to the very large range of atomic number between Al, Cu and Au. Another interesting effect can be observed when the β-phase alloys are examined under conditions of Nomarski interference contrast. Solid state transformations in these samples produce a series of laths that can be seen to form an intricate "basket weave" type structure with associated surface relief. The very small differences in height produce light that is slightly out of phase with that reflected off a smooth surface. The difference is then converted to bright colours by the Nomarski optics, Figure 6. These colours are, however, artefacts of the microscope and are not present in the actual sample, a point that has caused some misunderstanding in the jewellery industry in the past.

It is also interesting to note that there is a change in measured colour in Spangold as a result of the transformation to the spangled finish. This is noted by Wolff [18] who provided a colour chart showing the CIE a^* and b^* colour coordinates of Spangold as a function of Al content and heat treatment. This change has the net effect of causing the alloy to have a greater yellow tinge at lower Al contents and a redder hue at higher contents. Luminance (L) also decreases after spangling. Although colour of metals derives in the first instance from their electronic structure [23], we do not believe that the change in the colour of Spangold is primarily attributable to a change in electronic structure. Rather, the change in measured colour in this case is produced by the roughening of the surface, which attenuates the reflection of the white light source of the colour measuring instrument, thereby reducing luminance and de-saturating the three colour channels. The net effect is a darker but more deeply coloured surface.

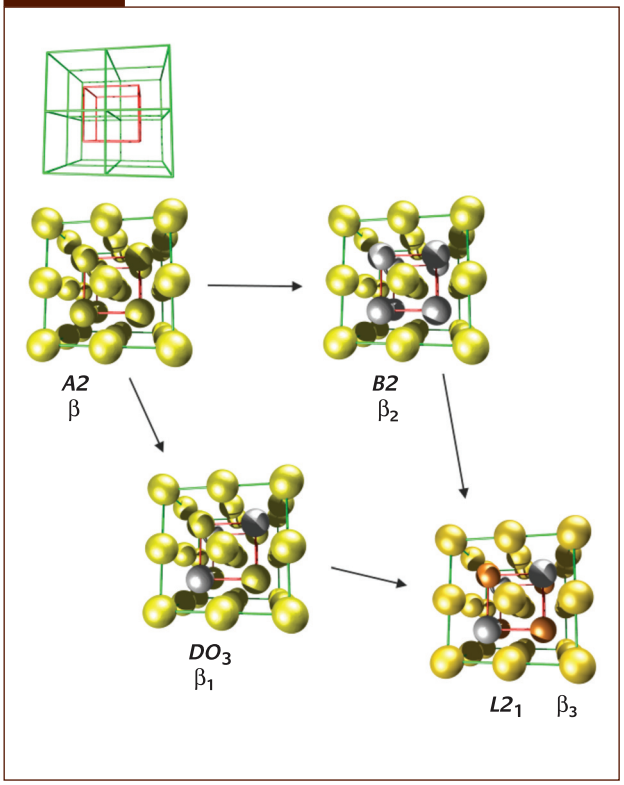
Crystal structure of the β-phases

A SMA has the unique ability to recover its shape after it has been plastically deformed through a diffusionless rearrangement of the atoms in the crystal lattice. This occurs due to the alloy having two stable phases, a high temperature parent phase known as austenite and a low temperature phase known as martensite. As the alloy is cooled strain is placed on the lattice until it passes through a critical transformation point at which point the lattice will become distorted by a diffusionless shear transformation and form martensite. This is then reversible when the temperature increases, with the atoms "remembering" their original position, thereby restoring the crystal lattice (and shape) of the austenite.

The crystal structures of the parent and martensite phases are an important aspect of shape memory alloy technology. In general almost all useful SMA systems have a parent phase that is packed in the body-centred cubic fashion and which is chemically ordered to some extent, while the martensite phase is closest packed, usually with some highly faulted scheme that produces a comparatively large unit cell. The volume change between bcc and closest-packed is about 6% in ideal circumstances and it is this change in density that produces the lattice strain in SMAs. There are, however, many possible candidate crystal structures for both the high and the low-temperature condition. The structure of the parent and martensite phases in the β-phases of the Al-Au-Cu system is an important question that has not yet been completely resolved. However, it is known that the parent β-phase of Spangold has the $L2_1$ body-centred packing arrangement [20] when at a temperature a few tens of degrees Celsius above the A_s, i.e. between about 100 to 120°C [20]. This structure is also found in the parent β-phase of diverse Cu-based ternary SMAs, and other gold-based SMAs such as $Au_xCu_yZn_z$ [24]. The $L2_1$ structure consists of four interpenetrating fcc superlattices, A,B,C, and D, which together produce a 16 atom bcc unit cell. Two of the fcc lattices, say A and C, are identical. Compared to the *B2* structure, the $L2_1$ structure contains additional ordering (whereas in the *B2* structure the B and D superlattices would be identical). This can be detected using X-ray and neutron diffraction because the additional atomic ordering produces superlattice lines. It is possible for the ordering in a ternary alloy (e.g. Cu-Au-Zn) to vary continuously between *B2* and $L2_1$, depending on composition and temperature [25]. A schematic illustration of these structures is shown in Figure 7. Overall, the packing is body-centred cubic but, in Spangold, the Au atoms tend to predominate on the A sites, the Cu atoms on the B sites and the Al on the C sites and the crystallographic symmetry becomes fcc.

It has been speculated that the $L2_1$ phase transforms to the less ordered *B2* phase at some higher temperature, and then, at about 630°C, to the *A2* structure [20, 26, 27], as in CuZn. If so, then the $B2 \rightarrow L2_1$ transition must occur somewhere between 120 and 630°C. There is, however, no compelling

Figure 7



Possible structures of the parent β-phase of copper- and gold-base shape memory alloys, classified according to Strukturbericht designations and the βi of Delaey[25]. The 16 atom superlattice is shown first, unpopulated. If all sites in the superlattice are occupied by the same element then the resulting structure is A2 (body centred cubic). If the red sites are occupied by a different kind of atom to the green sites then the structure is known as B2, which has AB stoichiometry and simple cubic symmetry. If only every other red site is occupied by a different kind of atom the structure is DO_3, with A_3B stoichiometry and fcc symmetry. Finally, if all the green sites are occupied by one kind of atom (gold, say) and two other kinds of atoms (copper and aluminium, for example) alternate on the red sites, then the stoichiometry is A_2BC (Au_2AlCu in this example) and the symmetry is fcc. Structures of intermediate nature can also exist, depending on the composition of the β-phase

calorimetric evidence for this transformation on cooling from 630°C, although a case has been made for it occurring at ~130°C when material that has been quenched from 630°C is reheated [26] (note however, that the exothermic reaction observed at 130°C could equally well have been due to the annealing out of previously quenched-in vacancies, a well-known phenomenon in SMAs). In any event, if the $B2 \leftrightarrow L2_1$ transition occurs in the range of 120°C to 630°C, its enthalpy is obviously so low that it has not been unambiguously detected yet. A low enthalpy for this transition is also found in other SMAs [27]. On the other hand, Gu *et al.* have placed the $B2 \leftrightarrow L2_1$ at 430°C on the basis of resistivity and internal friction measurements [27].

The structure of the martensitic phase is even more problematic. A hcp *B19*-like unit cell, doubled to account for the inherited ternary ordering, and with regular micro-twinning or stacking faults, has been proposed [29]. This would be consistent with the literature on AuCd, which is a far better-known gold SMA. Alternatively, others have proposed a large 18R-type monoclinic unit cell for the martensite on the basis of electron diffraction patterns [26], with a = 0.465 nm, b = 0.556 nm, c = 3.906 nm and α=87°, consistent with the usual situation for copper-base SMAs forming from an $L2_1$ parent. This has a fcc style of packing. Further complicating the matter is the fact that the structure of martensite formed is likely to depend on the *e/a* ratio anyway. In Cu-Al-Mn SMAs higher *e/a* ratios form a twinned *2H*-type, i.e. hexagonally packed *B19*-style, martensite, and lower *e/a's* form a fcc-packed *18R* one [30]. Further work is evidently required.

It has been found [26, 31] that freshly cast Spangold does not transform to martensite, at least not until it has been aged or annealed for a short time (several minutes) at a temperature in the range of 100 to 200°C. The explanation appears to be that, as in some copper-based SMAs, *e.g.* [32-34], the M_s is suppressed until a minimum degree of atomic ordering, whether $L2_1$ or DO_3, is developed in the β-phase. The ageing heat treatment provides the time and thermal energy needed to generate this critical minimum amount of ordering in the structure. Once ordered however, Spangold displays only a modest amount of the deleterious ageing effect known as 'martensite stabilization' [21, 35], a factor that distinguishes it from many copper-base SMAs.

Discussion: applications for ternary al-au-cu alloys

Shape Memory Alloys (SMAs)

The argument for future commercial application of Au-based SMAs would have to be based on them possessing attributes that are sufficiently attractive to overcome the cost of the raw materials they contain. We maintain that this is an entirely feasible proposition. The cost, for example, of implanting a stent or other device into a human body is so high that the use of a few grams of Au-based SMA hardly alters the economics. In this case a Au-based SMA would be feasible provided it provided some unique advantage, such a stable and precise transformation temperature or radio-opacity imparted by the high atomic number of Au. (Radio-opacity is desirable in some medical applications because it permits the manipulation of an implanted device to be followed *in vivo* and real time with low-dose X-ray radiation.) However, there appears to be no commercial exploitation of these alloys as SMAs yet.

Jewellery

Obviously, in the case of jewellery that is to be hall-marked, any SMA used in it should also be similarly hall-markable. SMAs can conceivably be used in jewellery in a clasping arrangement (the one way SME only!) or for the surface texturing effect, and indeed jewellery has, so far, been the

most commonly suggested application for Al-Au-Cu alloys. In fact, as we have shown, material properties favourable for use in jewellery are in general hard to accomplish in this ternary system, with most compositions producing silver or grey tones and brittle artefacts. The outstanding exception is the β-phase ternary alloy which can produce a range of colour from yellow to apricot-orange depending on its composition and which has reasonable mechanical properties. Wolff and Cortie have critically assessed the 18 carat Spangold alloy for its uses in gold jewellery, with properties such as colour, caratage, workability, castability and wear resistance being considered [18, 19, 36]. Spangold can be hot-rolled [27] but is, nevertheless, on balance, relatively hard and difficult to work. For example, it has a Vickers hardness of approximately 250 HV in the annealed state [22] compared to other 18 carat compositions which might be used at ~150 HV in the same condition. Therefore, very little cold work can be imparted to these alloys. Of course a figure of 250 HV is still substantially lower than the hardness of the 18 carat Al-Au-Cu γ-phase (~500 HV) which is also very brittle and silver coloured [22]. This effectively precludes use of the γ phase as a 'white gold' in commercial jewellery. Although the Spangold alloy had been licensed in the 1990s to manufacturing jewellers in Germany, France, South Africa and Mauritius, actual commercial production has been negligible.

Corrosion and tarnish resistance

Use of these alloys in both the medical and jewellery industries would require excellent resistance to corrosion or tarnishing. The Au-Cu alloys are excellent in this regard, at least down to about 15 carats. Spangold itself is known to tarnish in air, which causes a slight darkening of its colour [19]. The effect is due to the formation of a thin film of aluminium oxide. On the other hand, Spangold is resistant to corrosion in physiological liquids. The binary Au-Al β-phase, which is about 23 carats, is very resistant to corrosion. One of the present authors (FCL) wore a test ring of the Au-Al β-phase for several weeks without observing any tarnishing. $AuAl_2$ resists corrosion and discoloration if protected from abrasion. However, if $AuAl_2$ jewellery is subjected to wear and water it will develop a brass-coloured sheen that must be periodically removed using a cloth. This is because $AuAl_2$ is a relatively soft material (~200-250 HV [22]) and jewellery containing it must be treated gently, much like a pearl should be. Finally, little is known about the corrosion resistance of the remaining ternary compositions of this system.

Ductilizing of purple gold, $AuAl_2$

The properties and possible applications of the $AuAl_2$ compound [8] lie somewhat outside of the scope of this review. Nevertheless, it can be seen in the two phase diagrams provided that $AuAl_2$ can contain up to 5 at% Cu. Indeed additions of Cu have been claimed in patents as a means of modifying the colour [37] and ductility of $AuAl_2$ [38]. However, given the limited extension of the $AuAl_2$ phase field into the published 500°C ternary, additions of more than 5 at% Cu will be likely to generate brittle inclusions of the η , ζ, δ or γ intermetallic compounds. Furthermore, since η , ζ, δ or γ are silver-coloured, addition of Cu is also likely to cause a bleaching of the desirable purple colour of $AuAl_2$.

Dental alloys

An age-hardening α-phase Au-Cu-Al alloy containing 1.3 wt% Al and equiatomic amounts of Au and Cu has been patented and described [17]. A 60% increase in strength could be obtained by intraoral ageing at 37°C (*i.e.* the hardening took place in the mouth of the patient). These compositions should provide excellent resistance to corrosion in this environment.

Conclusions

Determination of the full Al-Au-Cu ternary phase diagram was not attempted until about 2000, and is not yet complete. Nevertheless, this system contains much of interest to both scientists and technologists. It has well-developed β and γ electron compounds, while several of its edge phases such as 'red gold' (Au,Cu), 'purple gold' ($AuAl_2$), and copper-aluminium shape memory alloy (Cu_3Al plus alloying elements) are of some technological interest. However, as far as its true ternary phases is concerned, most interest seems to have been focused on 'Spangold', an 18 carat shape memory alloy with potential applications in jewellery and radio-opaque medical implants. Spangold is resistant to the phenomenon of 'martensite stabilization' and hence has a comparatively stable range of transformation temperatures. Consideration of the phase diagram strongly suggests that additional, lower caratage SMAs can also be developed in this system.

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